Evidence for catalyst association in the catalyst transfer polymerization of thieno[3,2-*b*]thiophene

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ABSTRACT.

The performance of catalyst transfer polymerization (CTP) reactions which depend on catalyst association was studied on 3,6-dioctylthiothieno[3,2-*b*]thiophene (TT) monomers. This monomer was selected because a strong association of the catalyst is expected, since the aromaticity of thienothiophene is largely maintained when the catalyst and thienothiophene associate. This study includes both reported and unreported Ni- and Pd-catalyst systems. It is found that no polymer formation can be observed using Ni-catalysts, whereas Pd-catalysts show a similar behavior as for other monomer systems. During the study of the Ni-catalyzed CTPs, the π-associated Ni^0-complex has been isolated in situ and displayed a high stability in solution. It is shown that the associated complex interferes with the polymerization reaction and even prevents polymer formation. Furthermore, this complex prevented any Kumada-coupling reaction in the presence of the TT unit, as it serves as a "trapping site" for free Ni^0 catalyst entities. Ni^0-trapping

does not occur during polymerization of 3-alkylthiophene, confirming the presence of the π-associated Ni^0-complex in this polymerization. This introduces a new convenient method of probing Ni^0-association during all Ni-catalyzed reactions. Furthermore, these results establish the presence of an upper limit to the catalyst association strength -above which oxidative addition is prevented and the polymerization is inhibited- and they therefore add extra considerations for optimal catalyst design.

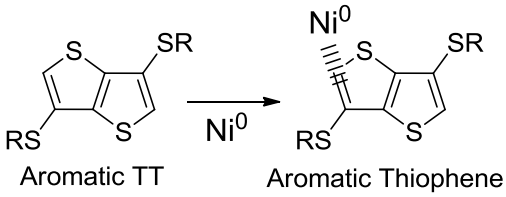
INTRODUCTION

Since the discovery of the first controlled chain-growth polymerization reaction of conjugated polymers a decade ago,[1,2] a tremendous amount of research has resulted in a significant understanding of the polymerization mechanism of conjugated polymers.[3–6] Different aspects which influence catalyst transfer polymerizations (CTP) such as catalyst optimization, ligand design, monomer selection, etc. have been investigated. In general, there are two ways of achieving a controlled chain-growth mechanism. The first method is based on a catalyst system which is released in solution but can only insert in a growing polymer chain, hereby excluding transfer reactions.[7–9] A second method is based on the association of the catalyst to the growing polymer chain during the polymerization in which the catalyst is transferred to a chain end (= CTP). The great majority of the developed polymerization mechanisms, whether they are based on a nickel or a palladium catalyst, rely to some extent on this catalyst association during the polymerization.[10–16] After the reductive elimination (RE) step, the catalyst is guided towards a terminal repeating unit by association with the π-system of the polymer backbone, where an oxidative addition (OA) occurs. The success or failure of this polymerization relies on the stability and lifetime of this catalyst association: it needs to be stable enough to ensure the OA and avoid catalyst dissociation, which can lead to chain termination (catalyst degradation) or

transfer reaction (reinsertion in monomer). This induces an interplay between the electronic properties of the catalyst and monomer, resulting in system-specific catalyst-monomer interactions, and can affect the polymerization behavior. This is represented in aspects such as the propagation rate of a polymerization and potential complications in the formation of block copolymers –an increasing association strength is necessary if the electronic properties of the blocks are sufficiently different.[17–21] Nevertheless, the association provides the control over the polymerization with a rather robust character by preventing any transfer reactions, even in the presence of transfer reagents. As a result, catalyst association during the polymerization can be determined indirectly by investigating the effect of purposely added transfer reagent.[15,22] Another way of determining catalyst association is by using a model coupling reaction between a monomer with organometallic entities and an aryl halide, in which a competition between inter- and intramolecular pathways is present; if catalyst association is present, the main products should be formed by intramolecular reactions. [10,12,13,23,24] Direct confirmation of the formation of an associated complex is not as straightforward, since in this case this species needs to be identified as the catalyst resting state to enable direct measurement thereof. Determination of the catalyst resting state is generally performed by *in situ* ^{31}P NMR measurements. In different reports regarding the Kumada catalyst transfer protocol (KCTP), both the RE and transmetalation (TM) have been stated to be the rate determining step under different circumstances, resulting in *in situ* isolation of a Ni^{II}-biaryl[25,26] or a Ni^{II}-aryl halide[27,28] complex resting state, respectively. Also, Senkovvsky *et al.* describe the presence of a mixture of several associated Ni^{0}-complexes in an anion-radical based polymerization of naphthalene diimide monomers with Ni(dppe)Cl_2.[29]

This report studies the behavior of association-dependent CTP on a thieno[3,2-*b*]thiophene (TT) monomer system. TT is a symmetric monomer consisting of two fused thiophene units (Scheme 1). Although TT has been studied in the synthesis of TT-homopolymers, it is mostly implemented in copolymers, as a donor entity in donor-acceptor copolymers or as a building block in dyes.[30–40] Almost all the TT-containing polymers have been synthesized electrochemically or through non-controllable step-growth polymerization mechanisms in which there is no catalyst association present during the polymerization. In one report, a KCTP polymerization resulted in uncontrollable formation of ill-defined oligomeric material. The report does not cover a mechanistic insight in this reaction, making the followed polymerization pathway unclear.[36] In copolymers, the TT-unit is often implemented without sidechains, but in the case of TT-homopolymers, these are obviously necessary for solubility reasons. Earlier research towards TT-homopolymer properties showed that the implementation of alkylthio sidechains on the TT-unit resulted in the most beneficial properties, with an optimized trade-off between polymer solubility and semi-crystallinity.[30] Hence, we focused on these alkylthio substituted TT-monomer entities for our investigations. In contrast to previously studied conjugated polymers, complexation of the Ni^0-catalyst with one part of the TT-monomer does not destroy the aromaticity of the whole monomer (Scheme 1). In fact, the annulation effect causes the loss in aromaticity to be only limited between the TT-system and thiophene. The aromaticity of one thiophene remains present, therefore, the complex can be expected to be much more stable in TT-monomers -similar as what is observed for other annulated systems (e.g. naphthalene, anthracene, indene, …).[25,41–45] This renders these systems particularly interesting towards studying their behavior in catalyst transfer polymerizations.

Scheme 1. Aromatic entities with and without the association with Ni^0.

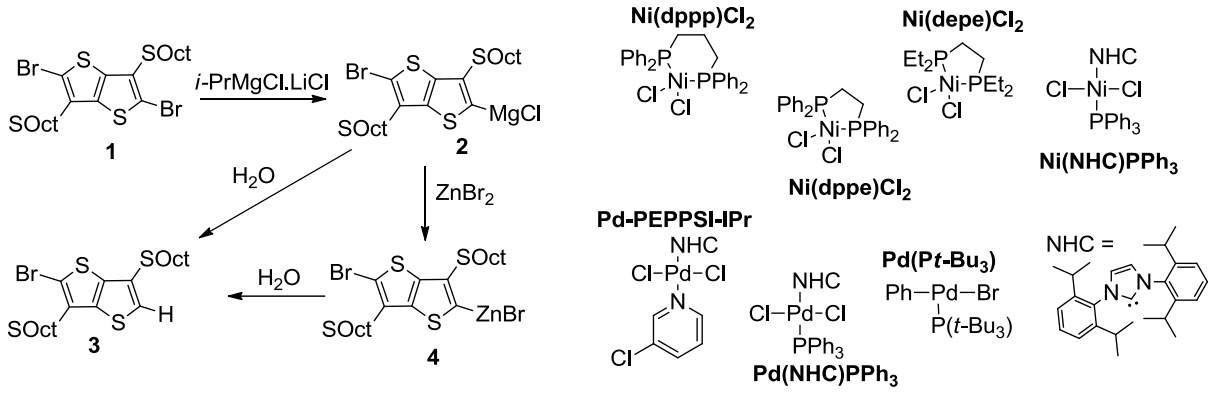


RESULTS AND DISCUSSION

Polymerization results

In the investigation of the polymerization properties, both nickel as well as palladium catalyst systems are considered. The nickel catalyzed polymerizations are based on the Kumada coupling reaction between a bromide and an organomagnesium substituted entity. The palladium catalyzed polymerizations that were performed, are based on the Negishi coupling reaction between a bromide and an organozinc entity. The synthesis of the 2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene precursor monomer (**1**) was performed as described in literature.[30] Starting from the precursor monomer (**1**) (Scheme 2), optimized GRIM conditions were established by comparing the chemical composition of H_2O quenched aliquots to a synthesized 2-bromo-3,6-dioctylthiothieno[3,2-*b*]thiophene reference (**3**) with ^1H NMR and ^{13}C NMR to ensure good and exclusive formation of the monoreacted monomer species (**2**)(Supporting Information, SI). Optimal results (>95% conversion) were obtained when using *i*-PrMgCl.LiCl as a Grignard reagent with a reaction time of 45 minutes and a concentration of 0.067 M. For all polymerizations using Ni-catalysts, this organomagnesium monomer (**2**) was used in the polymerization. For all performed Pd-catalyzed polymerizations, this organomagnesium monomer was first converted to the organozinc monomer (**4**) by a transmetalation reaction with 2 eq. of Schlenk-dried $ZnBr_2$.[7]

Scheme 2. Thienothiophene monomer formation reactions and overview of the different applied catalyst systems.



Being the most widely used catalyst system in a catalyst-associated controlled synthesis of conjugated polymers, we started our investigations using a Ni(dppp)Cl_2-catalyst. However, addition of monomer **2** to the Ni(dppp)Cl_2 catalyst does not yield any polymeric material. Recorded gel permeation chromatography (GPC) spectra clearly show that the main product that is present after the polymerization reaction can be ascribed to remaining monomer, although a small second peak at a slightly lower elution volume is observed (see further). Knowing that a Ni(dppp)Cl_2 catalyst results in a rate determining TM in the polymerization of thiophene and phenylene, we hypothesized that the reason for the inability to form polymeric material might be ascribed to this step.[27,28] However, switching to a Ni(dppe)Cl_2-catalyst, *i.e.* changing the rate determining step to the RE,[25] did not yield any polymer either, both at room temperature and 50 °C. These results indicated that the failure of the polymerization could not be ascribed to a hampering TM or RE in the polymerization cycle, leading towards the hypothesis that catalyst association might be the origin of the failure. In order to exclude that the association could be too weak – although a stronger association is expected- we investigated a catalyst system which associates stronger with the conjugated polymer, *i.e.* Ni(depe)Cl_2.[16,26] This catalyst showed no

improvement and did not lead to polymer formation. A last Ni-catalyst system that was selected was a Ni^{II}-N-Heterocyclic carbene (NHC) complex catalyst, used by the group of Mori in the polymerization of poly(3-hexylthiophene).[15,46,47] This catalyst system has also shown to polymerize through catalyst association, by yielding high molecular weights with no clear dependence on transfer agents (non-converted monomer).[15] Furthermore, the reactivity of this catalyst system has proven to differ significantly from other Ni-catalysts, which is reflected by a clear increase in reactivity towards thiophene with a Cl-atom instead of a Br-atom in the 2-position, in comparison with $Ni(dppe)Cl_2$. This difference in reactivity, however, had no effect on the polymerization of **2**: the Ni(NHC) complex did not succeed in forming any polymeric material. Given that the applied fundamental changes to the polymerization reaction in the KCTP by changing the catalyst ligand seemed to have absolutely no effect on the success of the polymerization reaction, it was tested whether changing the transition metal to palladium would result in polymer formation.

A first Pd-catalyst that was considered, was a Pd-PEPPSI-iPr complex, which is a popular catalyst in coupling reactions and is also capable of mediating catalyst-associated chain-growth polymerizations.[14,48,49] When combining monomer **4** with the catalyst, formation of polymeric material was observed, although a plateau in the molar mass was obtained at still very low values of around 2.4 kg/mol, theoretically corresponding to chain-lengths not higher than 6 units, with still large amounts of monomer remaining. Since Bryan *et al.* suggested that the "throw-away" ligand 3-chloropyridine might be responsible for the observed side-reactions in the polymerization of fluorene,[14,50,51] it was hypothesized that switching this ligand with a PPh_3 group might deliver better results. Through a "transligandation" reaction, the $Pd(NHC)PPh_3$ catalyst was readily obtained from the PEPPSI-IPr catalyst, as evidenced by ^{1}H, ^{13}C and ^{31}P

NMR (SI). This catalyst system resulted in the formation of some polymeric material, albeit with low molar mass and conversion and no improvement over the Pd-PEPPSI-IPr catalyst system was obtained. A final catalyst system that was used was a Pd(P*t*-Bu_3) catalyst. A phenyl-Pd(P*t*-Bu_3)-Br catalyst was prepared as described in literature and used in the polymerization of **4**.[52] Using this polymerization protocol, we were able to obtain polymeric material of TT with molar masses ranging up to maximum 8.5 kg/mol. If the polymerization is performed with a more soluble TT-monomer with 2-ethylhexylthio sidechains (EtHexS), similar molar masses are obtained, showing that the molar mass was not limited by solubility. Further investigation of the polymerization mechanism showed similar polymerization properties as described by Tkachov *et al.*[53] Polymer formation occurred very fast, with almost complete conversions at a polymerization time of 30 s. A chain extension experiment, in which a second equivalent was added after 5 min, showed that no further growth was obtained and no new polymer material was formed, suggesting chain termination and catalyst degradation occurred within the first 5 min of the polymerization. Because of the very fast polymerization, a potential linear $\overline{M}_n$-conversion relation could not be established to obtain insight into the growth mechanism before termination. However, it is shown that the used amount of catalyst influences the resulting molar mass -albeit significantly less then theoretically expected- indicating that the polymers are formed in a chain-growth mechanism (Figure 1). Furthermore, the catalyst-association during the polymerization was confirmed by the independence of the molar mass on the amount of transfer reagent (bromobenzene) used. From the polymerization results it can be concluded that the TT monomers behave in a comparable manner as other monomer systems with regard to catalyst systems in which palladium is used as the transition metal. However, polymerizations in which nickel is used as the transition metal systematically result in the inability to form any polymeric

material. This is especially peculiar since these Ni-catalysts have been studied much more intensively. A controlled polymerization is not always obtained, however in all reported research, some polymeric material is always recovered. For the TT-monomers on the other hand, none of the applied catalyst changes were effective, which indicates that the problem during the polymerization cannot be ascribed to the TM or RE, nor can it be ascribed to a too weak π-association of the catalyst. These results therefore urge further investigation to elucidate why it is observed that these Ni-catalyzed polymerization reactions fail to polymerize the TT monomer system.

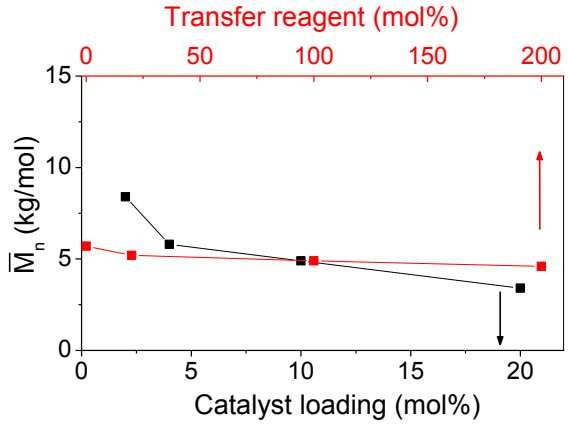


Figure 1. Influence of the catalyst concentration and the addition of transfer reagent on the molar mass of the TT-polymers synthesized using the Pd(Pt-Bu_3) catalyst. The transfer reagent studies were performed with a catalyst loading of 4 mol%.

Mechanistic KCTP study

As mentioned earlier, GPC spectra of the Ni(dppp)Cl_2 catalyzed CTP showed a signal that could not be ascribed to **2** or to catalyst entities. The molar mass of this signal corresponded to double the value found for the monomer signal (1.0 vs. 0.5 kg/mol) while maintaining a Đ-value of ±1.0, suggesting the formation of TT-dimers. Furthermore, the intensity of this signal proved to be dependent on the amount of catalyst that was used (Figure 2a), enforcing that a TT-dimer is

indeed formed in a coupling reaction with the Ni(dppp)Cl_2-catalyst. Moreover, when the integration values of the higher molar mass signal are compared, a linear increase in dimer formation in function of catalyst loading is found (Figure 2b), suggesting that each Ni(dppp)Cl_2 results in 1 dimer.

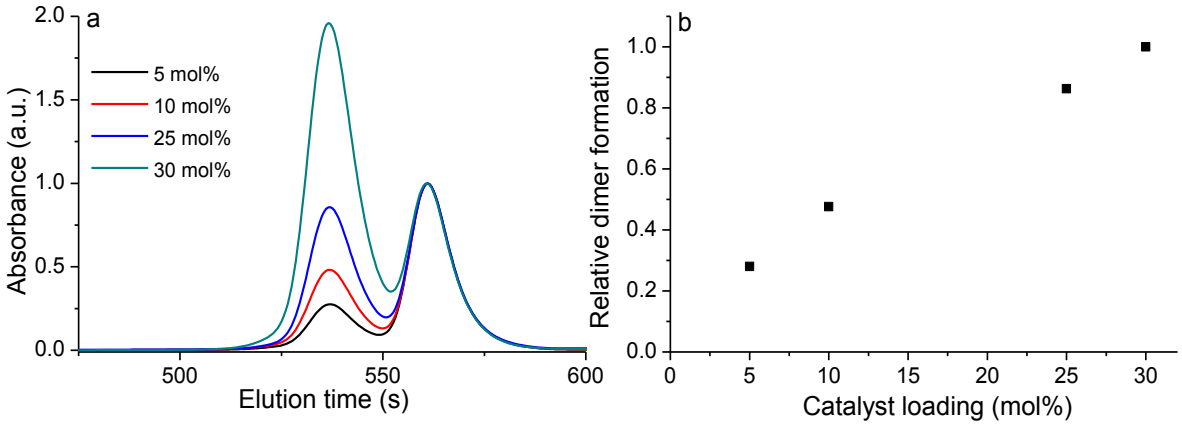


Figure 2. Influence of the catalyst loading on the outcome of the KCTP polymerization reaction with Ni(dppp)Cl_2. a) Systematic increase of the signal ascribed to the dimer in function of increased catalyst loading. b) Dimer formation in function of the catalyst loading, calibrated towards the integration value of the dimer signal in the experiment with 30 mol% of Ni(dppp)Cl_2.

These results imply that a CTP is initiated and that every catalyst entity indeed forms one TT-dimer. However, after the dimer formation the CTP stops and no further reaction is observed. Considering the mechanism of the coupling reaction, there are only a few different stages in which the polymerization reaction can be interrupted (Figure 3).

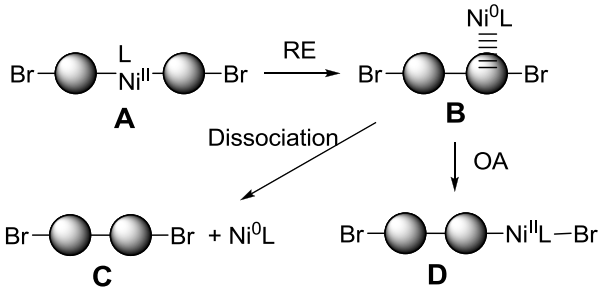


Figure 3. Overview of the different CTP intermediates that can lead to dimer formation.

Indeed, after quenching of the polymerization with acidified THF, there are two dimer entities that can be formed: a dibromo substituted TT-dimer in the cases **A**, **B** and **C**, or a monobromo substituted TT-dimer in case **D**. Isolation and characterization of the composition of the formed TT-dimers would therefore give a better insight into the reason of the CTP interruption. The dimer was isolated from the mixture by continuous washing with boiling methanol, which isolates the higher molar mass fraction as the insoluble remaining product (Figure S19, SI). Characterization of the dimer fraction with ^{1}H NMR, ^{13}C NMR and electrospray ionization-MS (SI) showed exclusive formation of the dibromo substituted dimer, excluding option **D** as the catalyst resting state, in which the reaction would be trapped before the TM step – i.e. before addition of the third TT-monomer. This result implies that the TM is not the rate determining step in the CTP of TT, in contrast with earlier attributed properties of the Ni(dppp)Cl_2 catalyst.[27,28] To distinguish between the three remaining potential intermediates and to determine which intermediate is responsible for the hampering of the CTP polymerization, *in situ* ^{31}P NMR measurements during the CTP reaction were performed. It is expected that the presence of intermediate **A** would result in one singlet peak, as the environment of both P-atoms is identical. This has also been shown by Lanni *et al*. in the case of a depe ligand with phenylene monomers.[26] In case **C**, the isolated Ni^0(dppp)-molecule would also yield one singlet peak, however, due to the instability of a free Ni^0-particle, further reaction of this entity with a second

Ni^0(dppp)-particle can occur, forming Ni and $Ni(dppp)_2$ which shows a singlet at 12.8 ppm relative to H_3PO_4.[54–56] The expected ^{31}P NMR spectrum in case **B** is less predictable, as this implies the isolation of the catalyst-associated intermediate, which is not common during a CTP reaction. Senkovskyy *et al*. reported *in situ* ^{31}P NMR measurements during an anion-radical based $Ni(dppe)Cl_2$ polymerization of a naphthalene diimide model system and obtained an associated complex which showed the presence of two doublets with a coupling constant (J_{PP}) of 28.3 Hz. Different, more complex ^{31}P NMR spectra were obtained during the polymerization, of which the observed signals were ascribed to the Ni^0(dppe) at different sites along the polymer chain.[29] Other stable associated complexes of comparable Ni^0-complexes with anthracene are also described in literature and consistently show the presence of two doublets with coupling constants around 65 Hz.[25,41] Monitoring the CTP of TT resulted in ^{31}P NMR spectra as shown in Figure 4, independent of the reaction time (10 min -3 h).

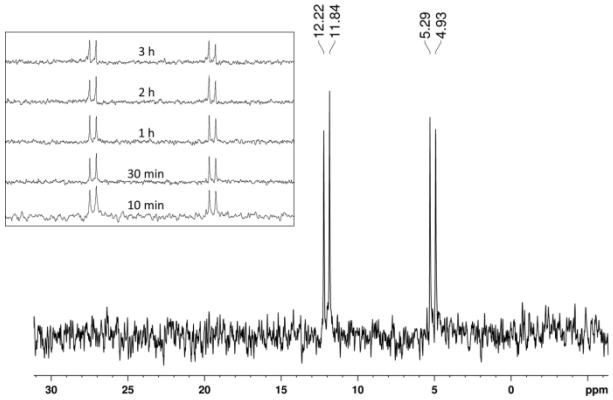


Figure 4. *In situ* ^{31}P NMR spectrum of the CTP of TT. The inset shows the reaction time independence. Spectra were measured in THF and calibrated towards a H_3PO_4 reference.

Considering the presence of two doublets with a coupling constant of ±62 Hz in the *in situ* ^{31}P NMR measurements, these results strongly indicate that the formed intermediate in the CTP reaction is indeed the associated complex **B**. Furthermore, it is shown that this complex is stable

in solution over a period of over 3 hours, without any oxidative insertion, regardless of the presence of two C-Br bonds. If the mechanism of the CTP is considered, the isolated dimer entity is the first species in the reaction that is confronted with the Ni^0-catalyst (Figure 5). It can be speculated that as soon as this Ni^0-entity is formed, immediate "trapping" of the catalyst occurs by the TT-π-system. This would mean that the association complex of the Ni^0-entity is much stronger in the case of TT compared to other monomer systems in which polymerization is obtained, as was anticipated. Indeed, as mentioned before, an explanation for this stronger association can be found in the molecular structure of the TT-monomer, being composed of two annulated thiophene units. Several papers have reported association complexes between a Ni-entity and annulated aromatic molecules such as η^2-naphthalene, η^3- and η^4-anthracene and also η^3-indene complexes, the latter being most related to the TT monomers.[25,41–44,57] It must also be mentioned that it can be excluded that the presence of the two alkyl sulfanyl groups is the origin of the strong association, since 3-alkylsulfanylthiophene monomers have already been successfully polymerized using $Ni(dppp)Cl_2$ as catalyst;[58–60] moreover, also the polymerization of dialkoxythienothiophene fails. Note that these experiments at this point cannot exclude that the absence of OA might originate from a hampering OA instead of a too strong complexation.

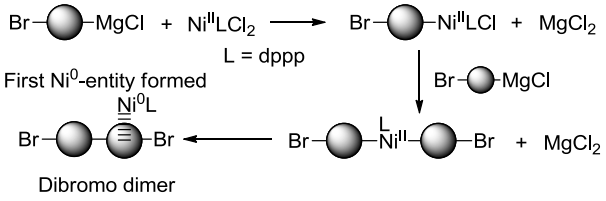
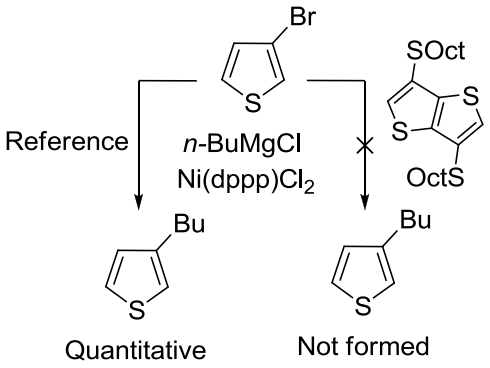


Figure 5. Representation of the isolated dimer as the first species that is confronted with the Ni^0 entity.

If it indeed is the case that thienothiophene forms a stable complex with a Ni^0-catalyst entity, the catalyst "trapping" should also hamper the envisioned coupling reaction in other types of

reaction in which these Ni^0-entities are used. In this context, it is peculiar that all described alkylation reactions of the TT-entity are consequently performed using Pd-catalysts, mostly using a rather elaborate 2 step procedure consisting of a Sonogashira coupling followed by a reduction of the triple bond[30,61] instead of using the Kumada coupling, which is typically used in the alkylation of for instance thiophene. In our hands, the Kumada coupling reaction of 3,6-dibromo-TT with *n*-butylmagnesium chloride failed to produce any 3,6-dibutyl-TT end-product. GC-MS showed that the main products that were obtained could be identified as being either the starting product or the product of a competing GRIM reaction (3-bromo-TT)(SI). To get more insight into whether the failure of the Kumada coupling in the case of 3,6-dibromo-TT could in this case also be ascribed to a Ni^0-"trapping", the effect of the presence of a TT-entity in a Kumada alkylation reaction of 3-bromothiophene with *n*-butylmagnesium chloride was investigated (Scheme 3).

Scheme 3. Kumada coupling reaction of alkyl groups with thiophene and the influence of TT on the reaction.



3,6-dioctylthio-TT was selected to mimic as closely as possible the TT-monomer present in the CTP experiments, while avoiding possible GRIM side-reactions with the TT-entity. The reference Kumada coupling of 3-bromothiophene with *n*-butylmagnesiumchloride and $Ni(dppp)Cl_2$ was monitored using GC-MS and a quantitative formation of the 3-butylthiophene

end product was obtained after a reaction time of 2 hours. The Kumada coupling reaction under the same reaction circumstances in the presence of 3,6-dioctylthio-TT resulted in no formation of the 3-butylthiophene (SI). Also in this case, the obtained results can primarily be ascribed to competing GRIM reactions, indicating the absence of any active Ni^0-catalyst species. These results further enforce the findings from the CTP reaction and illustrate again the Ni^0-"trapping" by the TT-molecules. This result also strongly indicates that not a hampering OA, but the too strong complexation, is the origin of the failure of the TT polymerization.

Considering this Ni^0-"trapping" by TT in the Kumada coupling reaction, the question arises what the effect of this TT-entity is on a KCTP polymerization reaction of 3-hexylthiophene. Therefore, a similar reaction approach as in the Kumada coupling was followed, but applied to the polymerization reaction (Scheme 4). The KCTP reaction yielded polymeric material with very comparable molar mass and polydispersity for the reference polymerization (**P3HT-ref**) and the polymerization reaction with the TT precursor monomer **1** present (**P3HT-TT**) (Table 1).

Scheme 4. KCTP of 3-hexylthiophene and the influence of TT on the polymerization.

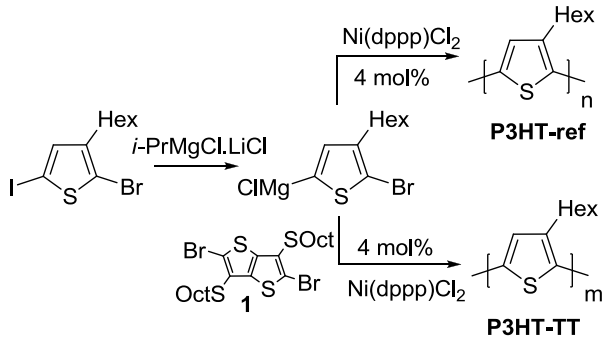


Table 1. Molar mass and polydispersity values for the synthesized P3HT polymers.

	$\bar{M}_n$ (kg/mol)	Đ
P3HT-ref	5.2	1.2

P3HT-TT	5.3	1.3

This means that in the case of the KCTP, no Ni^0-"trapping" is observed. While this might seem strange at a first glance -given the previous results of the alkylation reaction- an explanation can be found in a fundamental difference between both reactions (Figure 6). Indeed, in the alkylation reaction, the Ni^0-catalyst is formed by homocoupling of two *n*-butylmagnesium chloride molecules and is present as an unassociated particle in solution, before inserting in the C-Br bond of the next thiophene unit. This insertion reaction, however, competes with the formation of the associated Ni^0-TT complex and, as can be concluded from our results, the latter process takes the upper hand. In the KCTP mechanism on the other hand, the Ni^0-catalyst is formed after a first coupling of two thiophene monomer units. After the RE, the Ni^0-catalyst is not "trapped" by the TT because it is not present as an association complex with the thiophene dimer. From this association with thiophene, it undergoes the next OA and the regular KCTP mechanism continues. This experiment therefore further confirms the effective presence of a Ni^0-associated complex during the KCTP of 3-alkylthiophene. This also implies that the TT-entity can be used as a convenient tool to study mechanistic properties of all Ni-catalyzed reactions by probing the presence of free Ni^0-particles.

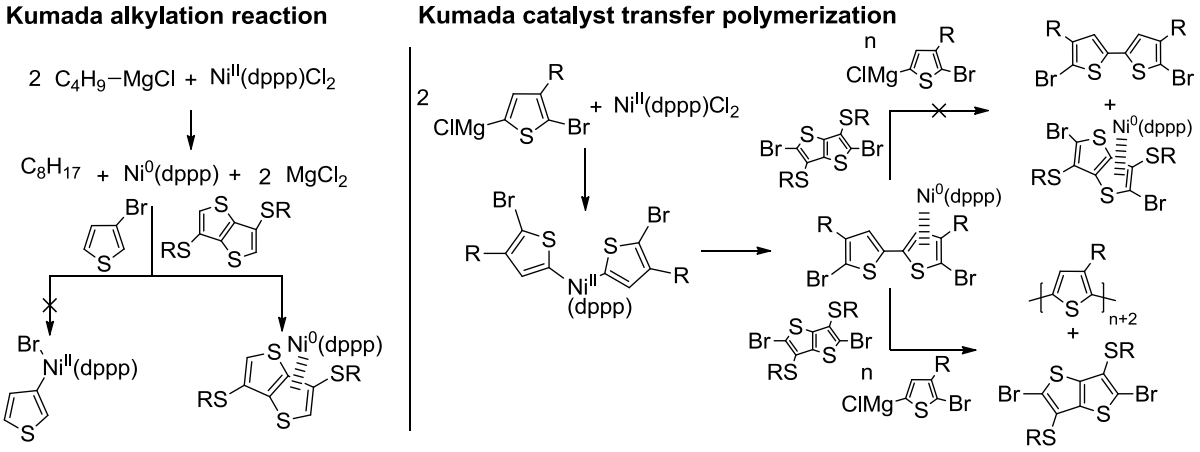


Figure 6. Mechanistic insight into the observed different reaction behavior between the Kumada alkylation reaction and the KCTP.

These results put the conventional interpretations regarding catalyst association in CTP into perspective. A stronger association has indeed showed promising results lately in the improvement of polymerization properties, especially towards electron deficient monomers, and hold great potential for further research.[16,26,62] The results presented in this paper do not oppose these findings, however they do show that care should be taken in the development of new catalytic systems, as the catalyst association strength has proven to show an upper limit, which prevents the OA, hereby hampering the polymer formation. The fact that we were unable to perform the KCTP with any of the used Ni-catalysts further shows that, besides the effects of the selected ligand, the π-system of the monomer entity has a crucial effect on the polymerization reaction. More in particular, other monomer systems containing annulated aromatic rings may be especially challenging to polymerize using the CTP protocols in which the catalyst entity is associated with the polymer chain. Moreover, also other Ni-catalyzed reactions of these annulated structures can be expected to be problematic. Further research towards the behavior of other annulated structures in Ni-catalyzed organic synthesis and polymerization reactions is currently being performed in order to further establish this hypothesis.

CONCLUSION

In this paper, catalyst transfer polymerizations are applied to a thieno[3,2-*b*]thiophene monomer system, which is selected in order to obtain a strong catalyst association with the monomer because of the remaining aromaticity of the associated catalyst-monomer entity. We demonstrate that polymerizations of TT are only possible by using palladium catalysts, which

tend to complex weaker with π-conjugated systems. A Pd(P*t*-Bu_3) catalyst yielded the best results (comparable with earlier reports on other monomers) and polymeric material with molar mass up to 8.5 kg/mol was obtained. The polymerization showed a very fast polymer formation (<30 s) with high conversion (>95%), although a controlled polymerization could not be established, as a chain extension experiment was unsuccessful. The molar mass of the resulting polymeric material was shown to be dependent on the amount of initiator and independent on the amount of transfer reagent, from which it was concluded that the polymers were formed through a non-controlled, association dependent chain-growth polymerization mechanism. Nickel catalysts in the CTP of TT-monomers, however, consistently fail to produce any polymeric material. It was found that dedicated changes of the ligand in order to fundamentally change the polymerization properties had no effect on the outcome of the CTP. Further investigation towards the reason of the failing Ni-catalysts showed the formation of a π-associated Ni^0-complex as soon as the Ni^0-entity is formed. This complex was shown to be stable in solution for over 3 hours. These results are in line with the strong association that was expected for these TT monomers Further results on Kumada alkylation reactions show that the TT entity serves as a "trap" of free Ni^0-entities. This Ni^0-trapping was not observed in the KCTP of 3-alkylthiophene, confirming the well-established hypothesis of the Ni^0-catalyst association complex during this polymerization. In addition, these results show that there is an upper limit in association strength, above which oxidative addition is hampered and no polymerization occurs, providing extra guidelines for future catalyst design.

ASSOCIATED CONTENT

Supporting Information. Reagents and Instrumentation, synthetic procedures, 1H, 13C and 31P NMR spectra as well as GPC spectra, mass spectra and GC-MS results are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org

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REFERENCES

(1) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(2) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.

(3) Yokozawa, T.; Ohta, Y. *Chem. Commun. (Camb).* **2013**, *49*, 8281–8310.

(4) Bryan, Z. J.; McNeil, A. J. *Macromolecules* **2013**, *46*, 8395–8405.

(5) Kiriy, A.; Senkovskyy, V.; Sommer, M. *Macromol. Rapid Commun.* **2011**, *32*, 1503–1517.

(6) Okamoto, K.; Luscombe, C. K. *Polym. Chem.* **2011**, *2*, 2424.

(7) Verswyvel, M.; Verstappen, P.; De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 5339–5349.

(8) Willot, P.; Steverlynck, J.; Moerman, D.; Leclère, P.; Lazzaroni, R.; Koeckelberghs, G. *Polym. Chem.* **2013**, *4*, 2662–2671.

(9) Verswyvel, M.; Steverlynck, J.; Hadj Mohamed, S.; Trabelsi, M.; Champagne, B.; Koeckelberghs, G. *Macromolecules* **2014**, *47*, 4668–4675.

(10) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(11) Tkachov, R.; Senkovskyy, V.; Komber, H.; Sommer, J.-U.; Kiriy, A. *J. Am. Chem. Soc.* **2010**, *132*, 7803–7810.

(12) Grisorio, R.; Mastrorilli, P.; Suranna, G. P. *Polym. Chem.* **2014**, *5*, 4304.

(13) Verswyvel, M.; Hoebers, C.; De Winter, J.; Gerbaux, P.; Koeckelberghs, G. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 5067–5074.

(14) Bryan, Z. J.; Smith, M. L.; McNeil, A. J. *Macromol. Rapid Commun.* **2012**, *33*, 842–847.

(15) Tamba, S.; Shono, K.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2011**, *133*, 9700–9703.

(16) Bridges, C. R.; McCormick, T. M.; Gibson, G. L.; Hollinger, J.; Seferos, D. S. *J. Am. Chem. Soc.* **2013**, *135*, 13212–13219.

(17) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022–1023.

(18) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(19) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polym.* **2007**, *19*, 684–699.

(20) Wu, S.; Bu, L.; Huang, L.; Yu, X.; Han, Y.; Geng, Y.; Wang, F. *Polymer (Guildf).* **2009**, *50*, 6245–6251.

(21) Willot, P.; Govaerts, S.; Koeckelberghs, G. *Macromolecules* **2013**, *46*, 8888–8895.

(22) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817–7823.

(23) Bryan, Z. J.; McNeil, A. J. *Chem. Sci.* **2013**, *4*, 1620–1624.

(24) Larrosa, I.; Somoza, C.; Banquy, A.; Goldup, S. M. *Org. Lett.* **2011**, *13*, 146–149.

(25) Lanni, E. L.; McNeil, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579.

(26) Lanni, E. L.; Locke, J. R.; Gleave, C. M.; McNeil, A. J. *Macromolecules* **2011**, *44*, 5136–5145.

(27) Lanni, E. L.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8039–8044.

(28) Tkachov, R.; Senkovskyy, V.; Komber, H.; Kiriy, A. *Macromolecules* **2011**, *44*, 2006–2015.

(29) Senkovskyy, V.; Tkachov, R.; Komber, H.; John, A.; Sommer, J.-U.; Kiriy, A. *Macromolecules* **2012**, *45*, 7770–7777.

(30) De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 568–578.

(31) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; Macdonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 328–333.

(32) McCulloch, I.; Heeney, M.; Chabinyc, M. L.; DeLongchamp, D.; Kline, R. J.; Cölle, M.; Duffy, W.; Fischer, D.; Gundlach, D.; Hamadani, B.; Hamilton, R.; Richter, L.; Salleo, A.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Zhang, W. *Adv. Mater.* **2009**, *21*, 1091–1109.

(33) Lim, E.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 4288–4293.

(34) Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Tuladhar, P. S.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I. *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275.

(35) Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. *Chem. Commun.* **2009**, 2198.

(36) Zhang, X.; Köhler, M.; Matzger, A. J. *Macromolecules* **2004**, *37*, 6306–6315.

(37) Zhang, X.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813–9815.

(38) Rutherford, D. R.; Stille, J. K.; Elliott, C. M.; Reichert, V. R. *Macromolecules* **1992**, *25*, 2294–2306.

(39) Taliani, C.; Zamboni, R.; Danieli, R.; Ostoja, P.; Porzio, W.; Lazzaroni, R.; Bredas, J. L. *Phys. Scr.* **1989**, *40*, 781–785.

(40) Danieli, R.; Taliani, C.; Zamboni, R.; Giro, G.; Biserni, M.; Mastragostino, M.; Testoni, A. *Synth. Met.* **1986**, *13*, 325–328.

(41) Stanger, A.; Vollhardt, K. P. C. *Organometallics* **1992**, *11*, 317–320.

(42) Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1475–1477.

(43) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233-234*, 157–176.

(44) Jiménez-Tenorio, M.; Puerta, M. C.; Salcedo, I.; Valerga, P.; Costa, S. I.; Silva, L. C.; Gomes, P. T. *Organometallics* **2004**, *23*, 3139–3146.

(45) Benn, R.; Mynott, R.; Topalovic, I.; Scott, F. *Organometallics* **1989**, *8*, 2299–2305.

(46) Fuji, K.; Tamba, S.; Shono, K.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2013**, *135*, 12208–12211.

(47) Tanaka, S.; Tamba, S.; Tanaka, D.; Sugie, A.; Mori, A. *J. Am. Chem. Soc.* **2011**, *133*, 16734–16737.

(48) Valente, C.; Belowich, M. E.; Hadei, N.; Organ, M. G. *European J. Org. Chem.* **2010**, 4343–4354.

(49) Valente, C.; Calimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 3314–3332.

(50) Chen, M.-T.; Vicic, D. A.; Turner, M. L.; Navarro, O. *Organometallics* **2011**, *30*, 5052–5056.

(51) Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, E. A. B.; O'Brien, C. J.; Lough, A.; Organ, M. G. *Chem. a Eur. J.* **2010**, *16*, 10844–10853.

(52) Stambuli, J. P.; Incarvito, C. D.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194.

(53) Tkachov, R.; Senkovskyy, V.; Beryozkina, T.; Boyko, K.; Bakulev, V.; Lederer, A.; Sahre, K.; Voit, B.; Kiriy, A. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 2402–2407.

(54) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203–2214.

(55) Chavez, C. A.; Choi, J.; Nesterov, E. E. *Macromolecules* **2014**, *47*, 506–516.

(56) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–23895.

(57) Benn, R.; Mynott, R.; Topalovic, I.; Scott, F. *Organometallics* **1989**, *8*, 2299–2305.

(58) Vandeleene, S.; Van den Bergh, K.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 5123–5131.

(59) Wu, X.; Chen, T.-A.; Rieke, R. D. *Macromolecules* **1995**, *28*, 2101–2102.

(60) Goldoni, F.; Iarossi, D.; Mucci, A.; Schenetti, L.; Zambianchi, M. *J. Mater. Chem.* **1997**, *7*, 593–596.

(61) Bijleveld, J. C.; Verstrijden, R. A. M.; Wienk, M. M.; Janssen, R. A. J. *Appl. Phys. Lett.* **2010**, *97*, 073304/1–3.

(62) Bridges, C. R.; Yan, H.; Pollit, A. A.; Seferos, D. S. *ACS Macro Lett.* **2014**, *3*, 671–674.

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